MODIFICATION OF LANGMUIR EQUATION TO PREDICT THE RETENTION OF SULFONATED POLYACRYLAMIDE POLYMER IN POLYMER FLOODING

by

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13588

Dissertation submitted in partial fulfilment of

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(PETROLEUM)

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CERTIFICATION OF APPROVAL

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Approved by,

……………………

(Dr Masoud Rashidi)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

…………………………………

MOHD NORHAFIZI BIN RAMLEE

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ABSTRACT

Polymer flooding is a process in Enhanced Oil Recovery (EOR) to improve volume of oil recovered. To improve the efficiency of oil recovery, water-based polymer, e.g hydrolyzed polyarcylamide(HPAM) and xanthan are injected in the water flooding process. It helps to reduce the water to oil mobility ratio, resulting higher oil recovered. Nowadays, synthetic polymer, e.g. HPAM, is the most commonly used in polymer flooding but it has some limitations. HPAM has limitation at high temperature above 75^{o}C and cannot be applied under high salinity. The other limitation that can influence and affect the performance of polymer flooding is retention. Retention is summation of mechanical entrapment, hydrodynamic retention and adsorption of polymer in porous media which contribute to reduce of polymer flooding efficiency. It is believed that by using different copolymer of polyarcylamide in polymer flooding, the retention effect may be reduced. By replacing some of carboxylate group of HPAM with another monomer,e.g. sodium salt of acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid (AMPS), effect of retention seem to be reduced.

The main aim of this study is to evaluate Langmuir equation whether the equation is applicable on sulfonated polyacrylamide polymer or not. The equation was analyzed and fitting parameters were extracted by using non linear fitting function of MATLAB software. Non linear fitting was used to tune the model parameters in order to obtain best fitting parameters. The result showed poor prediction ability of Langmuir isotherm if sulfonated polyacrylamide is used. The equation has already taken into account the present of divalent ions, permeability, temperature and polymer concentratiton but did not consider molecular weight and sulfonation degree parameters. Minitab software has been used to determine the significant of these parameters on the retention amount. The measurement was verified by using p-value and Pearson coefficient results. There was clear evidence that showed sulfonation degree has significant effect on retention amount of sulfonated polyacrylamide polymer in polymer flooding. Very low p-value (0.00) was achieved, which makes this parameter was reliable to be taken into account in modifying the Langmuir isotherm equation. The model outputs were validated by calculating the regression coefficient of MATLAB software.

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

This chapter is dedicated for introduction on study of retention phenomenon for sulfonated polyacrylamide polymer in polymer flooding. It covers the background of polymer flooding process and retention. The aim of the research work are justified and mentioned in this section.

1.1. Background of Study

Polymer is a compound made up from many repeating units (monomers) linked by chemical bonds [1]. Polymer plays important roles in Enhanced oil recovery (EOR) by increasing the viscosity of solution, results in increasing in sweep efficiency for enhanced oil recovery.

EOR is a tertiary recovery of oil production in which trapped oil left in the reservoir will be recovered using external energy. Polymer flooding is an example of EOR mechanism whereby water-soluble polymer is mixed to the water flooding [2].There are two main types of polymers that have been used in polymer flooding which are biopolymers and synthetic polymer. Xanthan is an example of biopolymer and hydrolyzed polyacrylamide is an example of synthetic polymer. Both of these polymers are commonly used in polymer flooding [3]. However, both Xanthan and HPAM have specific limitation.

HPAM has limitations at high temperature above 75^{o}C (HPAM hydrolyze at significant rate) and cannot be applied under high salinity [4]. On the other hand, xanthan is less sensitive towards the presence of divalent ions [5] but has injectivity problem with the present of cellular debris [6]. The other limitations for these polymers are adsorption and retention.

Polymer adsorption is expressed as polymer been trapped to the surface of rock in porous media [7]. Polymer adsorption occurred when there is inaccessible volume for polymer to pass through pore throat mainly due to smaller channel size and pore throat [8]. Polymer retention is mainly due to physical entrapment and chemical adsorption on formation surface [8]. Polymer and porous medium properties will be affected by the adsorption and retention of polymer [9].

According to Sheng[3], by replacing some of carboxylate group of HPAM with different copolymers, e.g. sodium salt of acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid (AMPS), the effects may be reduced. The sulfonated solution is used for the following reasons:

- AMPS has more stability in high temperature and salinity.
- AMPS has good capability in ionic exchange, electric conductivity and good resistance to divalence and salinity.

1.2. Problem Statement

Polymer retention reduces the performance of polymer solution in polymer flooding. Retention causes the total polymer loss in polymer solution [3]. Several factors such as temperature, concentration, molecular weight and sulfonation degree may affect the amount of polymer retention in porous media [10].

On the other hand, Langumir isotherm equation is currently used to measure polymer retention. The equation is available in commercial simulators such as Eclipse and UTCHEM [44]. The equation has not been tested for sulfonated polyacrylamide polymer so far.

1.3. Objectives

There are two main objectives need to be achieved;

1. To study the effect of several factors, i.e. temperature, present of monovalent and divalent ion, molecular weight and sulfonation degree on the retention phenomenon of sulfonated polyacrylamide polymer in polymer flooding.
2. To test the Langmuir isotherm equation with sulfonated polyacrylamide polymer and modify it if required.

1.4. Scope of Study

The scope for this project is to study the retention phenomenon of AMPS in polymer flooding. Research on the background of retention phenomenon of AMPS in polymer flooding from various sources such as journals and research papers has been carried out.

In this study, the main subjects under investigation are:

i. A relevant adsorption model, Langmuir isotherm equation has been identified to test the data file. Non linear fiiting function in MATLAB software been utilized in order to test the equation in order to predict retention amount of sulfonated polyacrylamide copolymers in porous media. The analysis on the model has been carried out and the model shows poor prediction measurement and been modified.

ii. The effect of different process variables such as sulfonation degree, temperature, present of monovalent and divalent ion and molecular weight parameters on the retention value also been presented. Minitab software has been used to determine the significant of these parameters on the retention amount of sulfonated polyacrylamide polymer.

iii. Modification of the model has been made by adding the parameter which has significant effect on retention value. The model outputs were validated through calculation of regression coefficient using MATLAB software.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1. General View of Polymer Flooding

There are three main stages in oil production; primary, secondary and tertiary oil production. Primary mechanism is the production by natural flow and artificial lift, see Figure 1. Secondary mechanism is mainly about pressure maintenance. The pressure is maintained by injecting external energy into the reservoir. Tertiary mechanism is oil recovery by the injection of materials not normally present in the reservoir (EOR) [11].

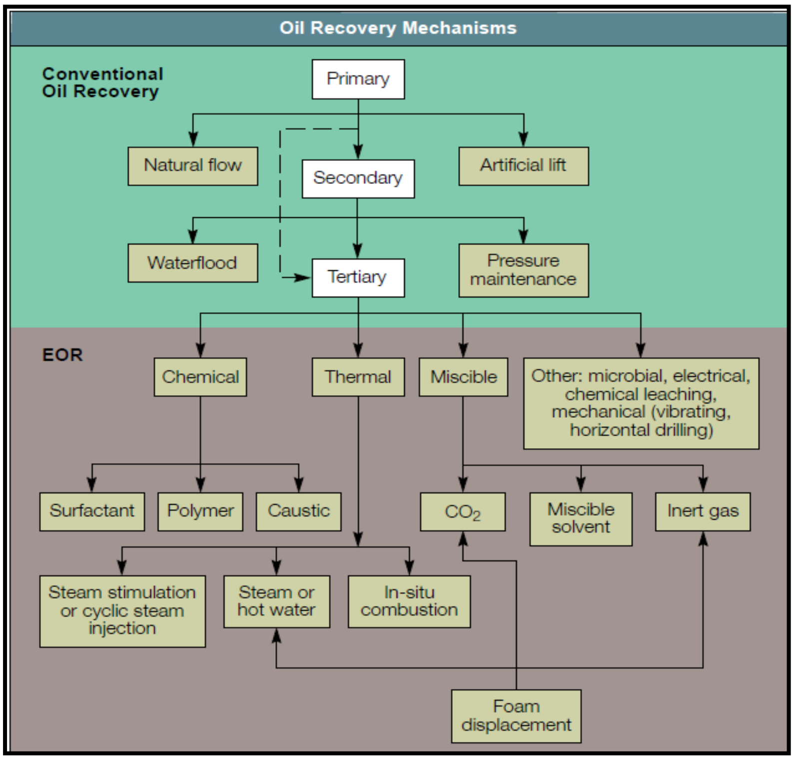

FIGURE 1. Oil Recovery Classifications [12]

Polymer flooding is considered as EOR method whereby water soluble polymer is added to water flooding process [2]. A complete explanation on the effect of changing mobility ratio on displacement efficiency in polymer flooding has been studied by researchers [12]. As the mobility ratio decreases, the displacement efficiency of oil increases and more oil can be recovered [12]. Mobility ratio is defined as mobility of displaced fluid over mobility of displacing fluid [13],

$$M = \frac{\frac{k}{\mu}\ (of\ displaced\ fluid)}{\frac{k}{\mu}\ \ (of\ displacing\ fluid)}$$

where M, k and μ are mobility ratio of displaced fluid to displacing fluid, effective permeability and viscosity respectively.

2.2. Several Definitions and Concepts

Below are definitions of some terms that may has been used in the project.

2.2.1. Polymer

Polymer is describes as substances made of more than one repeating units (monomers) by polymerization process. [14]. Some examples of polymer types, repeating units and monomers were shown in Figure 2.

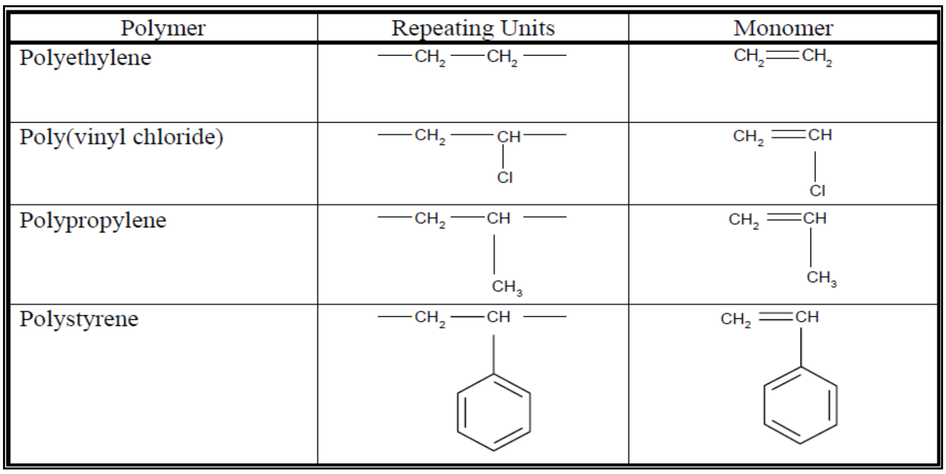

FIGURE 2 Examples of polymer,monomer and its repeating units [14]

2.2.2. Monovalent Ions

Monovalent ions are ions with single electric charges either positively-charged or negatively-charged [15] e.g Sodium ions (Na^+), and Chloride ions (Cl^-). Monovalent ions are formed by gaining or loss of single electron to the outer-most valence shell in a neutral atom [16]. Positively-charged monovalent ions (cations) are formed when an atom losses an electron meanwhile negatively charged monovalent ions (anions) are formed when an atom gain an electron [17].

2.2.3. Divalent Ions

Divalent ions are ions with two electrical charges either positively-charged cations or negatively-charged anions [16], e.g calcium ions (Ca^{2+}), Magnesium ions (Mg^{2+}) and Zinc ions (Zn^{2+}) . Thus, divalent ions can form two bonds with other ions or molecules [16], The presence of divalent in formation affects the salinity of the brines [18]. High salinity means the brine has high level of divalent ions [19].

2.2.4. Polyelectrolyte

Polyelectrolyte is a polymer with ionizable group either cations (positively-charged) or anions (negatively-charged) and it can dissociates in polar solvent by leaving charges on polymer [20]. The examples of polyelectrolytes presented in Figure 3.

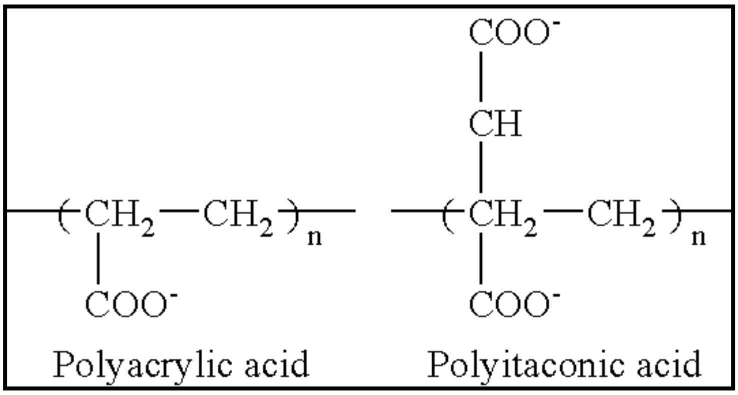

FIGURE 3 Examples of polyelectrolyte [20]

2.2.5. Sulfonated Polyacrylamide (AMPS)

Sulfonated Polyacrylamide is a polyelectrolyte with water-soluble anionic sulfonate. The molecular structure of AMPS is shown in Figure 4. AMPS also has shielding acrylamide and unsaturated double bond which make it less sensitive to the present of divalent ions and salinity [21]. AMPS also have good performance in high temperature condition [22].

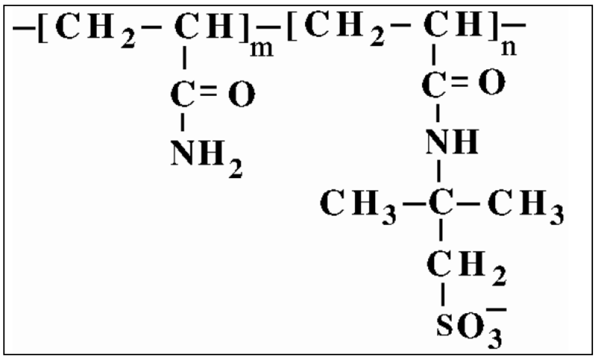

FIGURE 4 Molecular structure of Sulfonated Polyacrylamide [23]

2.2.6. Shear Rate

Shear rate is difines as the velocity difference between two layer of fluid or also known as velocity gradient [24]. Shear rate, γ formula;

$$\gamma = \frac{V\ (\frac{cm}{sec})}{X\ (cm)}$$

Where γ, V and X are shear rate, velocity difference between plates and distance separating plates respectively. See Figure 5,

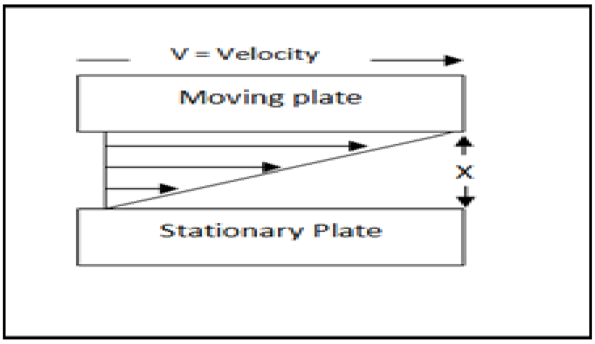

FIGURE 5: Simple shear flow [25]

The effect of shear rate on polyacrylamide adsorption have been discuseed by the researchers [26]. The effect of shear rate on polymer adsorption has been discussed in Table 1.

2.2.7. Mobility Ratio

Mobility ratio is defined as the ratio mobility of displacing phase divided by mobility of displaced phase [12]. The effect of mobility ratio on the areal sweep efficiency is study by [13]. Mobility ratio of waterflood will decrease if polymer is added to water (polymer flooding) as the viscosity of polymer solution will increase, results in greater sweep efficiency [31].

2.2.8. Polymer Viscosity

Viscosity is defines as a resistance to flow or in the simple word viscosity is equal to the ratio of shear stress over shear rate [32]. Some theories have been applied to explain the effect of viscosity on polymer retention [33]. The correlation between shear stress and shear rate which defined viscosity is shown in Figure 6.

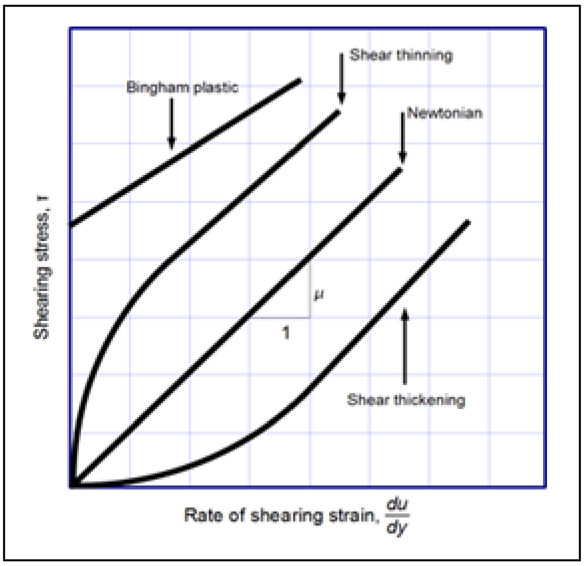

FIGURE 6 Viscosity from correlation of shear stress and shear rate. [32]

2.2.9. Langmuir Isotherm Equation

Langmuir isotherm equation was achieved by Langmuir in 1918. The equation is commonly used in describing chemical adsorption, such as polymer and surfactant adsorption [3]. General form of Langmuir equation is shown in Figure 7.

$$\hat{C}_i = \frac{a_P C_i}{1 + b_P C_i}$$

FIGURE 7 General form of Langmuir equation.[3]

where $\hat{C}_i$, C_i, is injected polymer concentration and adsorbed polymer concentration respectively and a_p and b_p are empirical constant.

Note that the Langmuir model is an equilibrium relationship, and its application assumes the process is in isothermal condition and homogenous in which the permeability is constant. [58]

2.2.10. P-value Coefficient

P-value is a method used to determine statistical significant in hypothesis test. It's to measure the 'significance' of empirical analyses [27]. The measurement is indicated by P-value ranges. Ranges of P-value are as shown in Table 1.

TABLE 1 Ranges of P-value coefficient [27]

$p < 0.001$	*highly significant*
$p < 0.05$	*statistically significant*
$0.05 < p < 0.1$	*low significant*
$p > 0.1$	*no significant*

2.2.11. Regression Analysis

The regression analysis is a method used to determine the relationship between the target and the output value. The range of regression is between –1 and +1, with positive numbers indicating a direct relationship (strong) and negative numbers indicating a weak relationship. A correlation of zero means there is no statistical relationship [28]. The simple linear regression equation,

$$y = ax + b$$

where variable a and b,

$$a = \frac{(\sum y)(\sum x^2) - (\sum x)(\sum xy)}{n(\sum x^2) - (\sum x)^2} \qquad b = \frac{n(\sum xy) - (\sum x)(\sum y)}{n(\sum x^2) - (\sum x)^2}$$

2.2.12. Root Mean Square Error (RMSE)

RMSE is used to measure the difference between predicted and observed value by comparing the closeness of modelled and observed values. It also used to measure how well the curve fits the data [29]. RMSE is defined as below:

$$\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i - \acute{y}_i)^2}$$

where $y_i, \acute{y}_i$ is the observed and modelled values respectively.

2.3. Polymer Adsorption and Retention

2.3.1. Polymer Adsorption

Polymer adsorption is the formation of covalent bonds between polymer and surface when both of them interact with one another [7]. Adsorption will cause the polymer loss in porous medium [35]. Polymer adsorption is occurred at static condition in which everything is static and there is no polymer flow.[30]

2.3.2. Polymer Retention

Polymer retention includes mechanical entrapment, hydrodynamic retention and adsorption [33]. Mechanical entrapment and hydrodynamic retention are related and take place in flow-through porous media (not static) [3]. The retention is represent in Figure 9.

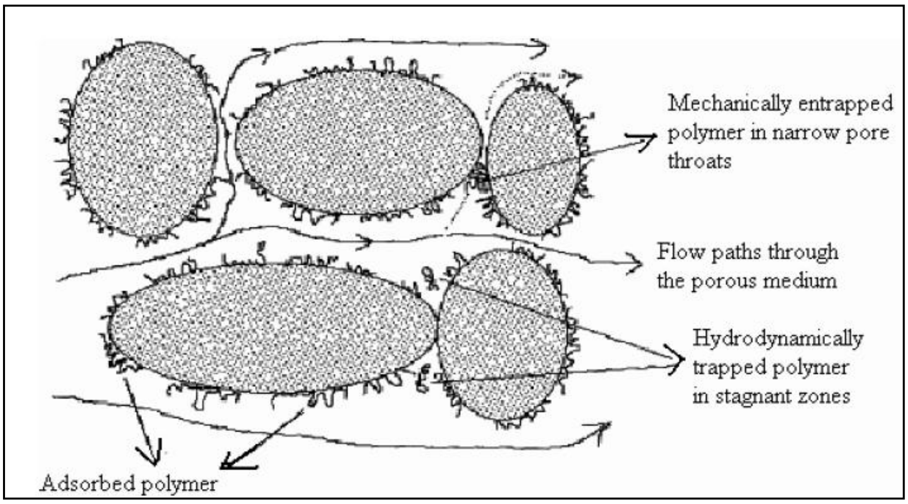

FIGURE 8 Polymer retention mechanisms in porous medium schematic diagram [9]

2.3.3. Polymer Adsorption and Retention Mechanism in Porous Media

Polymer adsorption is an accumulation of a material on solid matrix at a fluid-solid interface [36]. Adsorption of polymer onto clay surface reduces the displacement efficiency [37]. Polymer retention in porous media is due to adsorption onto the solid surfaces and trapping within small pores [37]. Table 2 shows the parameters affecting adsorption and retention of polymer.

TABLE 2 Parameter that effect Polymer adsorption and retention

Parameter	Effect on polymer retention	References
Wettability	Adsorption level is high in water-wet surface compared to oil-wet system.	[8]
	Retention decrease in oil-wet, increase in water-wet system.	[8]
Permeability	The higher permeability pack, the lower bridging adsorption and vice versa.	[38]
	When the sand permeability is low, retention level is high	[10]
Surface contact area	The greater surface area, the greater polymer adsorption. Fine-grained sand adsorbs more polymer than large-grained sand.	[35]
	Low pore size(high surface area) means that higher retention	[10]
Molecular Weight	High molecular weight(MW) polymer result in high adsorption compared to low MW	[39]
	High molecular weight (MW) polymer result in low retention of the polymer for both hydrolyzed and unhydrolyzed polyacrylamide	[40]

TABLE 2 Parameter that effect Polymer adsorption and retention (cont.)

Parameter	Effect on polymer retention	References
Polymer Concentration	Adsorption increases as the polymer concentration increases.	[41]
	Retention is higher when concentration of polymer is higher	[10]
Salinity	As salinity increases, retention increases.	[11]
Shear rate	Low shear rate means high flow resistance, results in high retention	[10]
	The adsorption increases as the shear rate increases.	[26]
Temperature	Adsorption decreases as the temperature increases.	[42]
Sulfonation degree	The higher sulfonation degree, the rate of hydrolysis decreases meaning retention is lower	[43]

2.4. Model Review And Development

2.4.1. Model Review

Langmuir isotherm is an equilibrium relationship, and its application assumes adsorption is instantaneous and reversible in terms of polymer concentration [3]. It is based on these hypotheses:

- The surface of the adsorbent is uniform and adsorption of all sites is equal. The adsorption is a bulk phenomenon in which the substance absorbed is uniformly distributed throughout the body of a solid or liquid.
- Adsorbed molecules do not interact between adjacent sites. The molecules do not collide with each other.
- All adsorption occurs through the same mechanism

2.4.2. Model Development

Model development is used to predict and describe some event or relationship (Kuhn, 2013). For the modelling of adsorption, the conventional Langmuir-type isotherm is commonly used. The Langmuir isotherm theory is a favourable tool for modelling the adsorption process [58]. Broad ranges of software have used this isotherm in developing the adsorption process. Commercial simulators such as CMG, Eclipse, UTCHEM, etc used this model to measure polymer adsorption

.

CHAPTER 3

METHODOLOGY

3. METHODOLOGY

3.1. Introduction

This chapter discuss the method used to test and modify the Langmuir equation based on the parameter has significant effect on retention amount of sulfonated polyacrylamide. Data file was extracted and tested with Langmuir equation using MATLAB. The equation was analyzed whether it is applicable on sulfonated polyacrylamide or not and fitting parameters were extracted by using non linear fitting function of MATLAB software. Figure 9 shows the flow chart for the project.

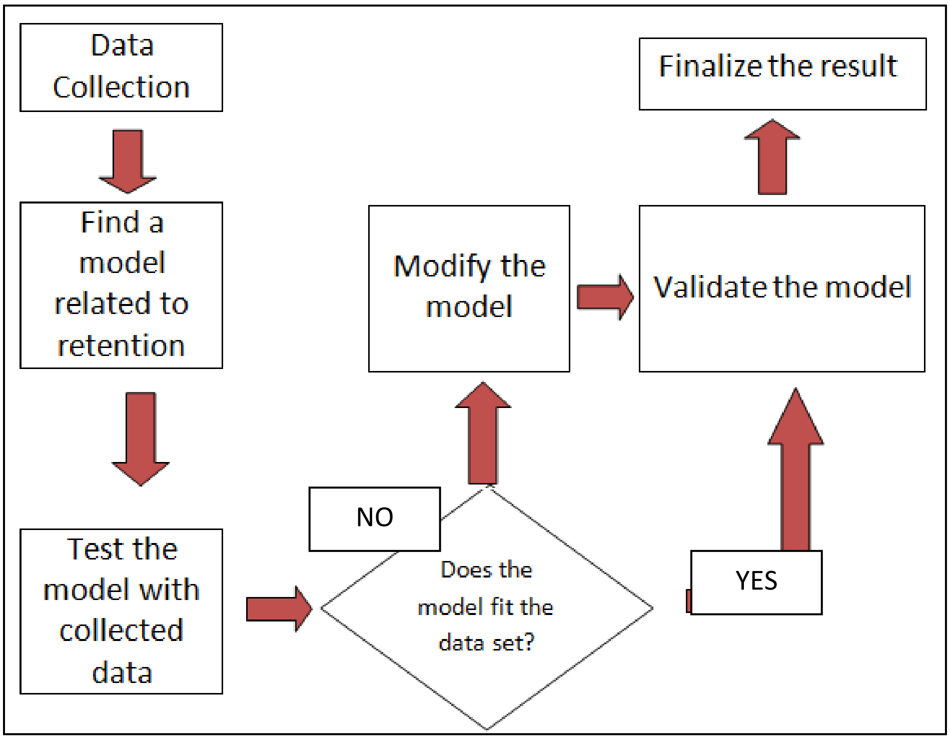

FIGURE 9 Flow Chart of the project

Data of retention of sulfonated polyarylamide polymer were collected from previous experimental study. Then after collecting the data, a suitable model which is related to the retention is required. After searching, Langmuir isotherm equation is considered as the best equation for this study. Cuong [44] in his paper mentioned that this model is favourable for modeling the polymer adsorption process. Then the model was tested with the collected data to confirm whether it is applicable on the polymer or not by using non linear function in MATLAB which has be discussed in the next section. If the equation suit with the data set, then we proceed with the validation of the model. If not, the model needs to be modified in order to adjust to suit the data set. After modify the model, the model need has been validated and the result has been finalized.

3.2. Data Gathering

Previous experimental studies have been reviewed and after confirmation, data has been extracted as shown in Table 3. Model for polymer adsorption which considered the parameters of the collected data is needed to validate and support the study.

TABLE 3 Data collected from literature

Polymer type	Core Type	Solution type	Concentration (ppm)	temperature (°C)	Molecular Weight (MDa)	Sulfonation Degree (mole %)	retention amount (μg/g)
AN105	Berea Sandstone	5 wt % NaCl	5000	20	6	5	93.43
AN105	Berea Sandstone	Synthetic Seawater	5000	20	6	5	111.46
AN105	Berea Sandstone	Synthetic Seawater	5000	80	6	5	111.7
AN113	Berea Sandstone	5 wt % NaCl	5000	20	8	13	29.48
AN113	Berea Sandstone	Synthetic Seawater	5000	20	8	13	58.64
AN113	Berea Sandstone	Synthetic Seawater	5000	80	8	13	60
AN125 VLM	Berea Sandstone	5 wt % NaCl	5000	20	2	25	32.45
AN125 VLM	Berea Sandstone	Synthetic Seawater	5000	20	2	25	38.96
AN125 VLM	Berea Sandstone	Synthetic Seawater	5000	80	2	25	46.8

TABLE 3 Data collected from literature (cont.)

AN125	Berea Sandstone	5 wt % NaCl	5000	20	8	25	7.36
AN125 VHM	Berea Sandstone	5 wt % NaCl	5000	20	12	25	1.29
AN125 VHM	Berea Sandstone	Synthetic Seawater	5000	20	12	25	3.23
AN125 VHM	Berea Sandstone	Synthetic Seawater	5000	80	12	25	10.5
AN132	Berea Sandstone	5 wt % NaCl	5000	20	8	32	6.76
AN132	Berea Sandstone	Synthetic Seawater	5000	20	8	32	16.48
AN132	Berea Sandstone	Synthetic Seawater	5000	80	8	32	20
HPAM	Berea Sandstone	1 wt % NaCl	5000	20	8	0	52.49
HPAM	Berea Sandstone	5 wt % NaCl	5000	20	8	0	108.92
HPAM	Berea Sandstone	Synthetic Seawater	5000	20	8	0	124.2
HPAM	Berea Sandstone	Synthetic Seawater	5000	80	8	0	139

3.3. Core Sample Description

The retention data is collected from previous experimental study. The polymer solution is injected into the Berea sandstone core. The core sample is 10 cm in length with the diameter of 3.7 cm as shown in Figure 10. The sulfonated polyacrylamide polymer is used as the polymer in simulation of polymer flooding.

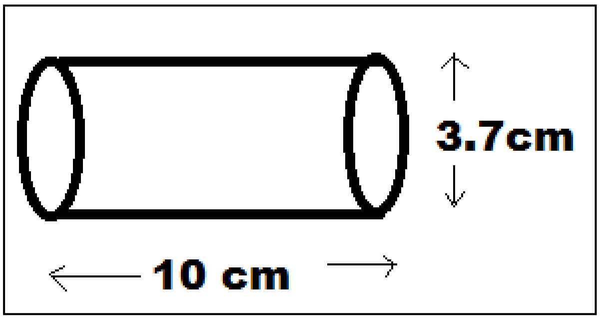

FIGURE 10 Size of core sample

Pore Volume (PV) is defined by Pepper [46],

$$PV = \frac{\pi D^2}{4} \times l \times \phi \quad (1)$$

$$= \frac{\pi (3.7)^2}{4} \times 10 \times 0.2$$

$=21.504\ cm^3$

where D, l, ϕ are core diameter, length and porosity of the Berea sandstone sample consecutively. Details about the core sample can be found in [45]. The bulk density = 2.32 g/cm^3 and the grain density = 2.772 g/cm^3 as mentioned in [46] .

The weight of rock/sand can be determined by

$$weight\ of\ rock = pore\ volume\ of\ core\ sample \times grain\ density \quad (2)$$

$$weight\ of\ rock[g] = cm^3 \times \frac{g}{cm^3}$$

$$weight\ of\ rock[g] = 21.504 cm^3 \times 2.772 \frac{g}{cm^3}$$

= 59.60 g of rock

and the weight of the polymer can be determined by

$$weight\ of\ polymer\ = retention\ amount \times weight\ of\ rock \quad (3)$$

$$weight\ of\ polymer\ = \frac{\mu g\ of\ polymer}{g\ of\ rock} \times g\ of\ rock$$

$$= 93.43 \frac{\mu g\ of\ polymer}{g\ of\ rock} \times 59.55 g\ of\ rock$$

= 5563.756 µg of polymer

The retention amount measured in the laboratory as (µg) need to be converted into Ĉp(ppm)

$$x[ppm] = \frac{0.005563756\ \mathrm{g}\ polymer \times 10^6}{995 g\ of\ brine + (0.005563756\ \mathrm{g}\ polymer)} \quad (4)$$

= 5.591683808 ppm

3.4. Generalized Langmuir Isotherm Equation

Langmuir isotherm theory is used in this study to model the polymer adsorption. This model is been used in the several commercial simulator such as CMG and Eclipse to measure polymer adsorption. The model also can be interpreted in the function of salinity, polymer concentration and permeability. The adsorbed concentration polymer is given by equation below

$$\hat{C}_p = min\left(C_p, \frac{a_p(C_p-\hat{C}_p)}{1+b_p(C_p-\hat{C}_p)}\right) \tag{5}$$

where C_p and $\hat{C}_p$ is the injected polymer concentration and adsorbed polymer concentration respectively. C_p - $\hat{C}_p$ is the equilibrium concentration in the rock polymer solution. The unit for b_p must be reciprocal of the unit of C_p. $\hat{C}_p$ must be same unit as C_p. The minimum adsorption value is taken to ensure that the adsorption is no greater than the total polymer concentration. a_p and b_p are the fitting parameters. The parameter a_p is defined as:

$$a_p = \left(a_{p1} + a_{p2}C_{sep}\right)\left(\frac{k_{ref}}{k}\right)^{0.5} \tag{6}$$

where (k_{ref}) and C_{sep} is the reference permeability and effective permeability respectively. The unit for a_p is dimensionless. Effective salinity for polymer, C_{sep} is defined by

$$C_{sep} = \frac{C_{51}+(ß_p-1)C_{61}}{C_{61}} \tag{7}$$

where C_{51},C_{61}, and C_{11} are the anion, divalent, and water concentrations in the aqueous phase respectively. $ß_p$ is the covalent coefficient.

3.4.1. Units

The laboratory unit used to define polymer retention, $\hat{C}_p$is in mass of polymer per unit mass of solid, usually in micrograms per gram of rock ($^{\mu g}/_{g}$). In the Langmuir adsorption model, the unit used for $\hat{C}_p$is in parts per million (ppm).

These units can be converted to each other according to the relationships.

$$\hat{C}_p = min\left[C_p, \frac{\left(\left(a_{p1}+a_{p2}\left(\frac{C_{51}+(ßp-1)C_{61}}{C_{61}}\right)\right)\left(\frac{k_{ref}}{k}\right)^{0.5}\right)(C_p-\hat{C}_p)}{1+b_p(C_p-\hat{C}_p)}\right] \quad (7)$$

$$\hat{C}_p[ppm] = min\left[C_p[ppm], \frac{\left(\left(a_{p1}+a_{p2}\left(\frac{C_{51}+(ßp-1)C_{61}}{C_{61}}\right)\right)\left(\frac{k_{ref}}{k}\right)^{0.5}\right)(C_p-\hat{C}_p)[ppm]}{1+b_p\left[\frac{1}{ppm}\right](C_p-\hat{C}_p)[ppm]}\right] \quad (8)$$

$= [ppm]$

As the unit for retention is $\frac{\mu g\ of\ polymer}{g\ of\ rock}$, it need to be converted into ppm.

3.4.2. Adsorbed Polymer Concentration (Ĉp)

Table 4 shows the amount of adsorbed polymer concentration (Ĉp) in parts per million.

TABLE 4 Adsorbed polymer concentration

Retention(µg)	Ĉp(ppm)
93.43	5.591684
111.46	6.670752
29.48	1.764353
58.64	3.509547
32.45	1.942104
38.96	2.331721
7.36	0.44049
1.29	0.077206
3.23	0.193313
6.76	0.404581
16.48	0.986315
52.49	3.141477
108.92	6.518737
124.2	7.433221

3.4.3. Equilibrium Concentration in the Rock Polymer Solution ($\mathbf{C_p - \hat{C}_p}$).

The equilibrium concentration in the rock polymer solution is measured by subtracting the injected polymer concentration and adsorbed polymer concentration ($C_p - \hat{C}_p$). Table 5 shows the equilibrium concentration in rock polymer solution.

TABLE 5 Equilibrium concentration in rock polymer solution

Cp(ppm)	Ĉp(ppm)	$C_p - \hat{C}_p(ppm)$
5000	5.591684	4994.408
5000	6.670752	4993.329
5000	1.764353	4998.236
5000	3.509547	4996.49
5000	1.942104	4998.058
5000	2.331721	4997.668
5000	0.44049	4999.56
5000	0.077206	4999.923
5000	0.193313	4999.807
5000	0.404581	4999.595
5000	0.986315	4999.014
5000	3.141477	4996.859
5000	6.518737	4993.481
5000	7.433221	4992.567

3.4.4. Present of Anion, Divalent and Water Concentration in Solution

In laboratory experiments, there are three types of solution used in the study, which are 1wt% of NaCl, 5wt% of NaCl and synthethic water. Different solutions consist of different amount of anion, divalent and water concentration present in the solution. Table 6 shows the amount of anion, divalent and water concentration present in particular solution. Following example shows how to calculate equivalent parts per million (ppm) from the original data based on weight %.

$$1wt\%\ NaCl = \frac{1g\ of\ NaCl}{1g\ NaCl + 99g\ water} \tag{9}$$

1wt% NaCl = 10000 ppm

$$5\text{wt\% NaCl} = 5\text{wt\%} * 10000\ \frac{\text{ppm}}{\text{wt\%}}$$

$$= 50000\ \text{ppm}$$

TABLE 6 Amount of anion, divalent, and water concentration in solutions

Solution	C_{51}(anion concentration	C_{61}(divalent concentration)	C_{11}(water concentration)
1wt% NaCl	10000	0	990000
5wt% NaCl	50000	0	950000
Synthethic Water	24747	12320	962900

Note that the Langmuir model consider the permeability to be properly distributed along the reservoir in homogenous manner, thus the value for $\frac{k_{ref}}{k}$ is assumed to be 1.

3.5. Test the Model with Collected Data

In order to determine whether the Langmuir model can be used for sulfonated polyacrylamide or not, the model is tested using the collected data using non linear fitting in MATLAB software. Based on the result, the model shows poor prediction result for sulfonated polyacrylamide and been modified based on parameter that has considerable effect on retention of sulfonated polyacrylamide in polymer flooding.

3.6. Evaluate the Effect of Sulfonation Degree, Present of Divalent and Monovalent Ion, Temperature and Molecular Weight on Retention of Sulfonated Polyacrylamide Polymer

The effect of sulfonation degree, present of divalent and monovalent ion, temperature and molecular weight has been evaluated using Minitab software. Minitab software has been used to determine the significant of these parameters on the retention amount. The measurement was verified by using p-value and Pearson coefficient result.

3.7. Modify Model Based on Parameter that has Significant Effect on Retention of Sulfonated Polyacrylamide

The Langmuir model has been modified with parameter that has significant effect on polymer retention based on the p-value obtained in the Minitab software. Regression analysis is carried out to validate the result.

3.8. Key Milestone

The approach of this project is based on examination and understanding of the scope of work and the timing for the completion of the project. In accordance with the milestones provided in the guideline for final year project, several key milestones have been identified and summarized for FYP I and FYP II in Table 7 and Table 8 respectively.

TABLE 7 Key Milestone for FYP I

Key Milestone	Proposed Week
Submission of Extended Proposal	Week 6
Proposal Defence	Week 9
Submission of Interim Report	Week 14

TABLE 8 Key Milestone for FYP II

Key Milestone	Proposed Week
Submission of Progress Report	Week 8
Pre-SEDEX	Week 11
Submission of Dissertation (soft bound)	Week 13
Submission of Technical Paper	Week 13
Oral Presentation	Week 14
Submission of Project Dissertation (hard bound)	Week 15

3.9. Gantt Chart

FYP I

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Topic Selection/ Confirmation														
2	Preliminary Research Work														
3	Submission of Extended Proposal Defence														
4	Proposal Defence(Oral Presentation)														
5	Project work continues														
6	Submission of Interim Draft Report														
7	Submission of Interim Report														

FYP II

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work Continues															
2	Submission of Progress Report															
3	Project Work Continues															
4	Pre-SEDEX															
5	Submission of Draft Final Report															
6	Submission of Dissertation															
7	Submission of Technical Paper															
8	Viva															
9	Submission of Project Dissertation															

CHAPTER 4

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

4.1. Results

This chapter describes the results obtained using the Langmuir and modified Langmuir model. It is composed of three main sections. The first section explains the simulation result of Langmuir model. The model has been interpreted by using regression analysis. The next section discussed on the effect of different process variable such as polymer concentration, sulfonation degree, temperature, molecular weight and salinity on polymer retention. The last section explains the modified Langmuir model after confirmation that the original Langmuir model needs to be modified. The validation method used to validate the model outputs also been discussed in this section.

4.1.1. Langmuir Model

From the data of experimental study, there were two temperature considered in the study which are 20^{o}C and 80^{o}C. As the Langmuir model is an isotherm model in which the temperature of the tested run is constant, the data must be run separately. As the data collected consists of two different temperatures, the calculation is done separately. The data used for 20^{o}C and 80^{o}C are shown in Table 9 and Table 10.

TABLE 9 Run for temperature @ 20oC

temperature	Retention	Run	Cp(ppm)	Ĉp(ppm)	Cp-Ĉp(ppm)	C51(ppm)	C61(ppm)	C11(ppm)	ß	Csep
20	93.43	1	5000	5.591683808	4994.408	50000	0	950000	2	0.052632
20	111.46	2	5000	6.670752486	4993.329	2.47E+04	1.23E+04	9.63E+05	2	0.038495
20	29.48	4	5000	1.764352666	4998.236	5.00E+04	0	9.50E+05	2	0.052632
20	58.64	5	5000	3.509547482	4996.49	2.47E+04	1.23E+04	9.63E+05	2	0.038495
20	32.45	7	5000	1.942104268	4998.058	5.00E+04	0.00E+00	9.50E+05	2	0.052632
20	38.96	8	5000	2.331721196	4997.668	2.47E+04	1.23E+04	9.63E+05	2	0.038495
20	7.36	10	5000	0.440490258	4999.56	5.00E+04	0.00E+00	9.50E+05	2	0.052632
20	1.29	11	5000	0.077205522	4999.923	5.00E+04	0.00E+00	9.50E+05	2	0.052632
20	3.23	12	5000	0.193313028	4999.807	2.47E+04	1.23E+04	9.63E+05	2	0.038495
20	6.76	14	5000	0.404580741	4999.595	5.00E+04	0.00E+00	9.50E+05	2	0.052632
20	16.48	15	5000	0.986314605	4999.014	2.47E+04	1.23E+04	9.63E+05	2	0.038495
20	52.49	17	5000	3.141477066	4996.859	10000	0.00E+00	9.90E+05	2	0.010101
20	108.92	18	5000	6.518737405	4993.481	5.00E+04	0.00E+00	9.50E+05	2	0.052632
20	124.2	19	5000	7.433221129	4992.567	2.47E+04	1.23E+04	9.63E+05	2	0.038495

TABLE 10 Run for temperature @ 80oC

temperature	Retention	Run	Cp(ppm)	Ĉp(ppm)	Cp-Ĉp(ppm)	C51(ppm)	C61(ppm)	C11(ppm)	ß	Csep
80	111.7	3	5000	6.685116113	4993.314884	2.47E+04	1.23E+04	9.63E+05	2	0.038495171
80	60	6	5000	3.590941879	4996.409058	2.47E+04	1.23E+04	9.63E+05	2	0.038495171
80	46.8	9	5000	2.800936878	4997.199063	2.47E+04	1.23E+04	9.63E+05	2	0.038495171
80	10.5	13	5000	0.628416691	4999.371583	2.47E+04	1.23E+04	9.63E+05	2	0.038495171
80	20	16	5000	1.196983492	4998.803017	2.47E+04	1.23E+04	9.63E+05	2	0.038495171
80	139	20	5000	8.31897602	4991.681024	2.47E+04	1.23E+04	9.63E+05	2	0.038495171

Langmuir Isotherm

Poor prediction result of Langmuir Isotherm (Temperature @ 20^{o}C)

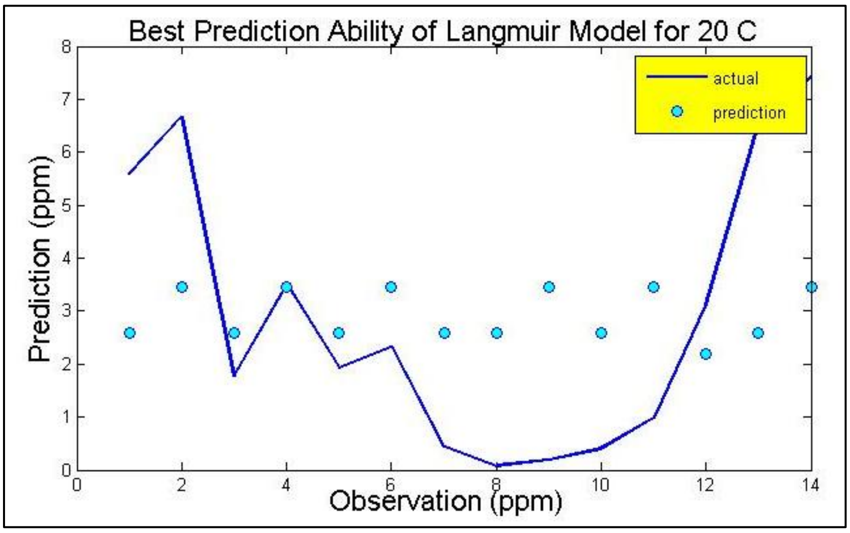

FIGURE 11 Prediction ability of Langmuir model for 20^{o}C.

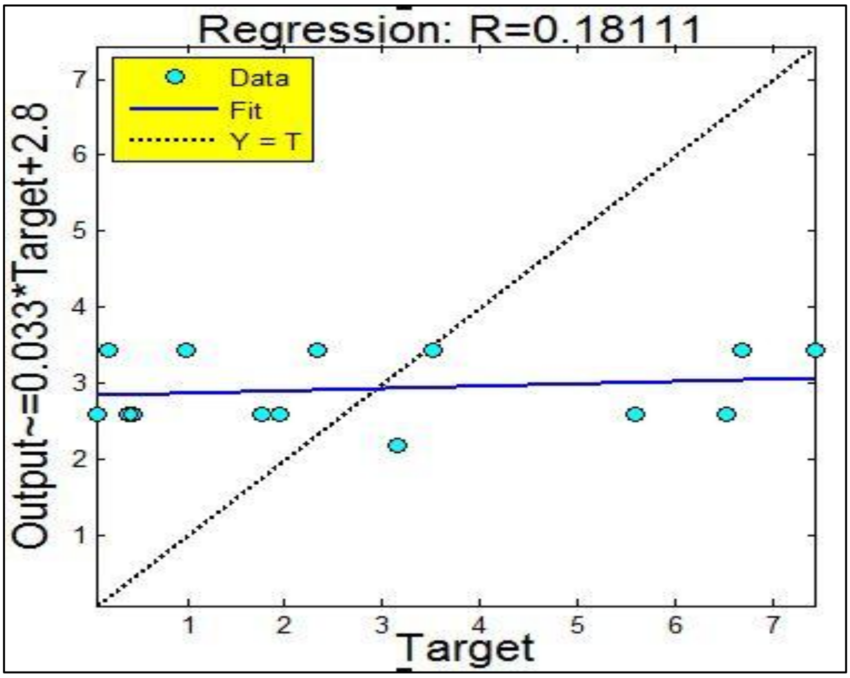

FIGURE 12 Regression for Langmuir model @ 20^{o}C

Poor prediction result of Langmuir Isotherm (Temperature @ 80^{o}C)

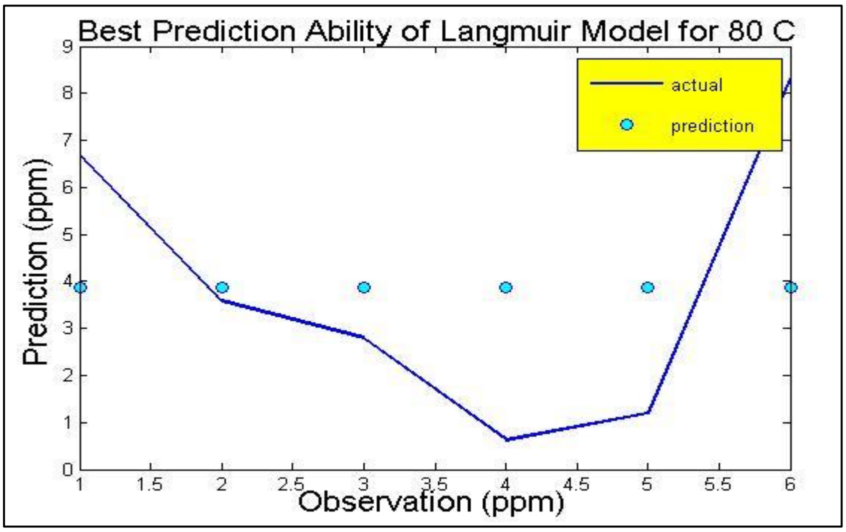

FIGURE 13 Best prediction ability of Langmuir model for 80^{o}C

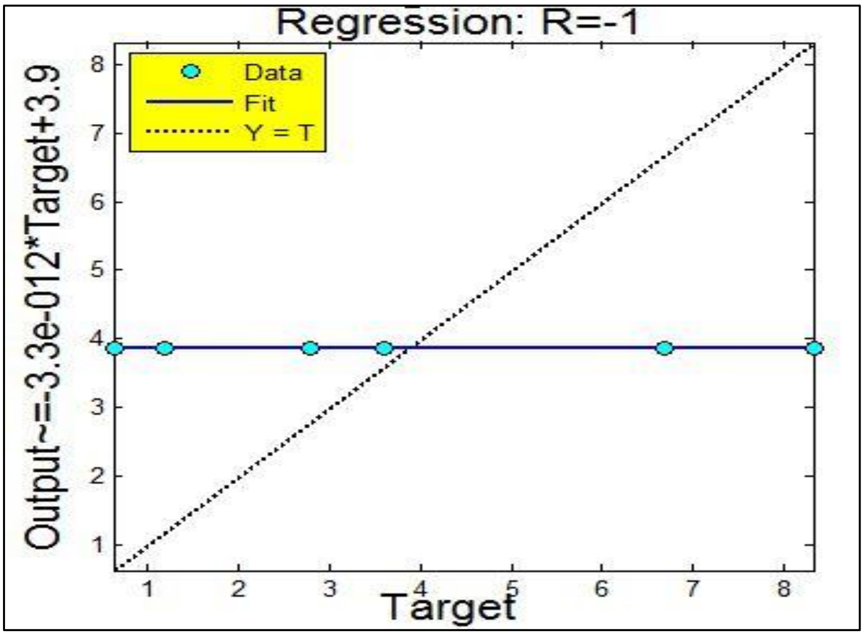

FIGURE 14 Regression for Langmuir model @ 80^{o}C

4.1.1.1. Langmuir Model Interpretation

The result of the Langmuir model showed the same trend for both temperature of 20^{o}C and 80^{o}C. Figure 11 and Figure 13 show result for best prediction ability provided by existing Langmuir model at temperature of 20^{o}C and 80^{o}C respectively. As results show significant difference between observations and model outputs, this means model is not able to forecast retention amount of sulfonated polyacrylamide when it is used as tested polymer. The interpretation indicates that the model should be modified by including some of the parameters which may affect the amount of retention of the polymer.

4.1.1.2. Regression of Langmuir Model

As shown in Figure 12 and 14, the linear regression coefficient is 0.1811 and -1 for the temperature of 20^{o}C and 80^{o}C respectively. This poor result of developed model means lack of fit.

4.1.2. Effect of Sulfonation Degree, Temperature, Molecular Weight, Concentration and Salinity

Based on the literature, sulfonation degree temperature, molecular weight, concentration and salinity may have effects on the polymer adsorption amount [10,11,39,40,41,42,43]. In this section, it determines how much these parameters affect the adsorption amount. The effect of these parameters is determined by the p-value and Pearson coefficient using statistical software MiniTab.

Figure 15,which has been extracted from statistical software, shows the effect of polymer concentration, sulfonation degree, temperature, molecular weight and salinity on polymer retention. The result shows the effect of sulfonation degree is greater than other parameters. P-value of sulfonation degree is close to zero which point to a great effect on the retention amount. Thus, sulfonation degree needs to be taken into account and may inserted to the Langmuir isotherm equation for providing a better results in terms of prediction ability.

On the other hand, molecular weight does not has great effect on retention of sulfonated polyacrylamide polymer as it shows p-value greater to be more than 0.05.

Results for: Worksheet 1

Correlations: retention am, Sulfonation , temperature , Molecular We, ...

	retention amount	Sulfonation Degr	temperature (°C)
Sulfonation Degr	-0.873		
	0.000		
temperature (°C)	0.163	0.023	
	0.492	0.922	
Molecular Weight	-0.255	0.023	-0.015
	0.278	0.925	0.949
Divalent in solu	0.224	0.044	0.535
	0.341	0.855	0.015
Monovalent in so	0.220	0.063	0.533
	0.351	0.791	0.015

Cell Contents: Pearson correlation
P-Value

FIGURE 15 Pearson correlation and p-value of Sulfonation degree, temperature, molecular weight, diavelent ion and monovalent ion in solution

4.1.3. Modified Langmuir Model

In this section the modified form of the Langmuir isotherm has been presented which take into account the effect of sulfonation degree. The sulfonation degree parameter can be incorporated into a_p ,as the unit is dimensionless, as follows:

$$a_p = \left(a_{p1} + a_{p2}C_{sep} + a_4 x\right)\left(\frac{k_{ref}}{k}\right)^{0.5} \quad (10)$$

where the a_{p1}, a_{p2}, a_4 are the fitting parameter and x is the sulfonation degree percent. The coefficients are determined by using non linear regression analysis function of MATLAB software. The needed data given in Table 11 and Table 12 show the sulfonation degree for each run.

TABLE 11 sulfonation degree for 20^{o}C

Temperature (^{o}C)	Sulfonation Degree	Retention (μg/g)
20	5	93.43
20	5	111.46
20	13	29.48
20	13	58.64
20	25	32.45
20	25	38.96
20	25	7.36
20	25	1.29
20	25	3.23
20	32	6.76
20	32	16.48
20	0	52.49
20	0	108.92
20	0	124.2

TABLE 12 sulfonation degree for 80^{o}C

Temperature(^{o}C)	Sulfonation Degree	Retention (μg/g)
80	5	111.7
80	13	60
80	25	46.8
80	25	10.5
80	32	20
80	0	139

Modified Langmuir Isotherm - Temperature @20^{o}C

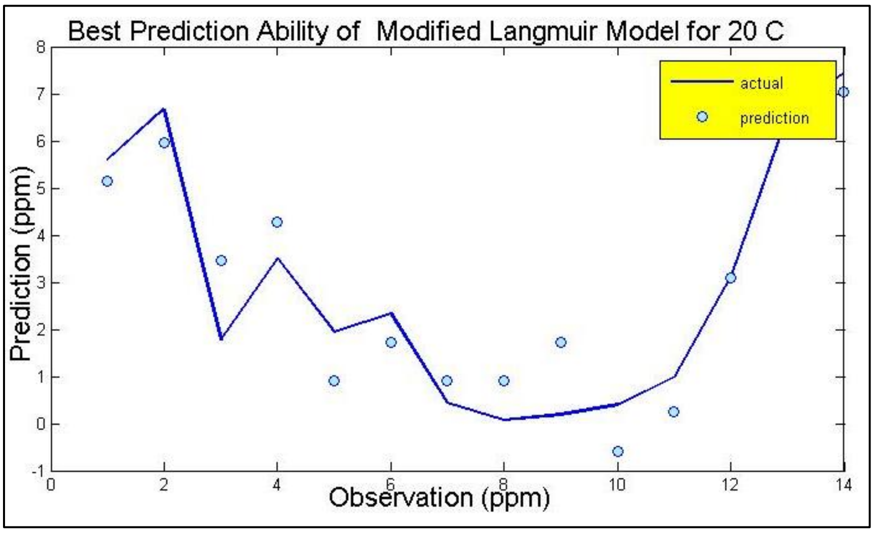

FIGURE 16 Best prediction ability of modified Langmuir model for 20^{o}C

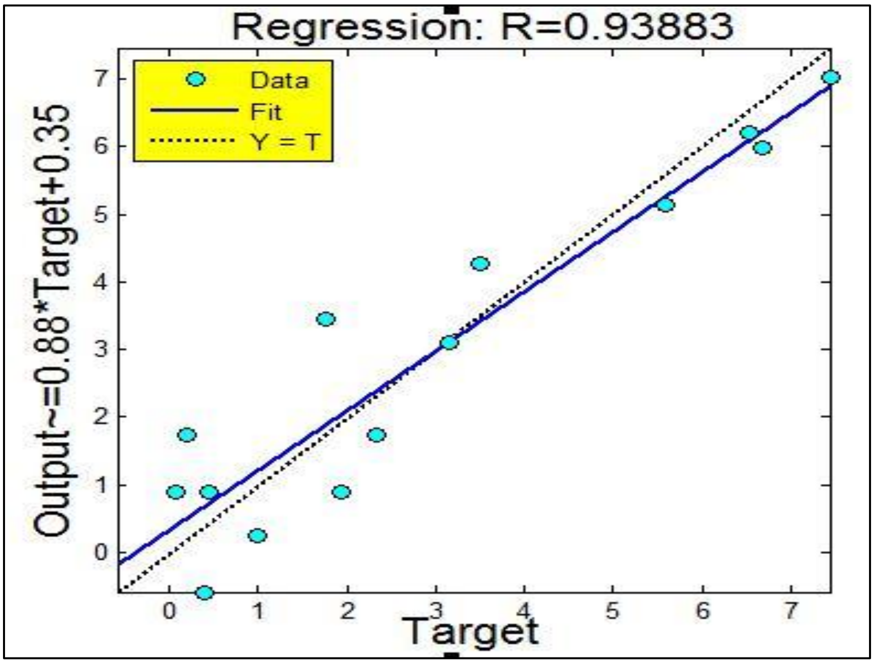

FIGURE 17 Regression for modified Langmuir model @ 20^{o}C

Modified Langmuir Isotherm - Temperature @80^oC

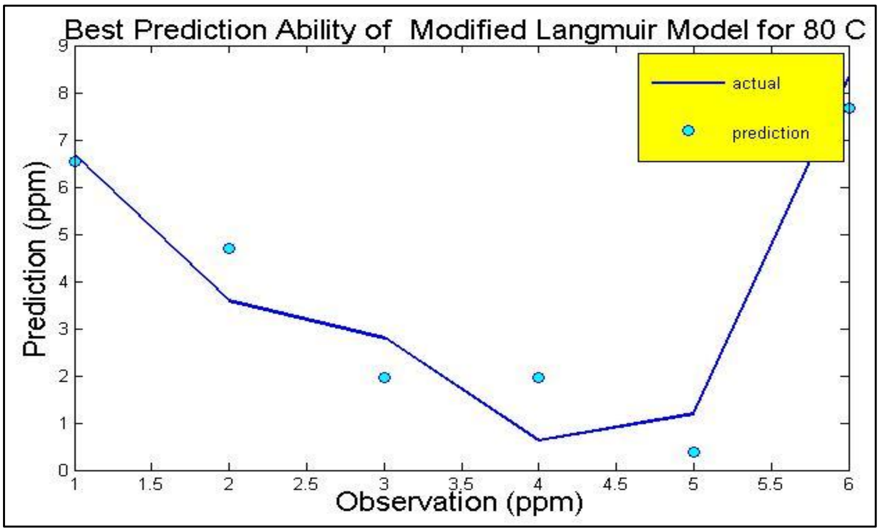

FIGURE 18 Best prediction ability of modified Langmuir model for 80^oC

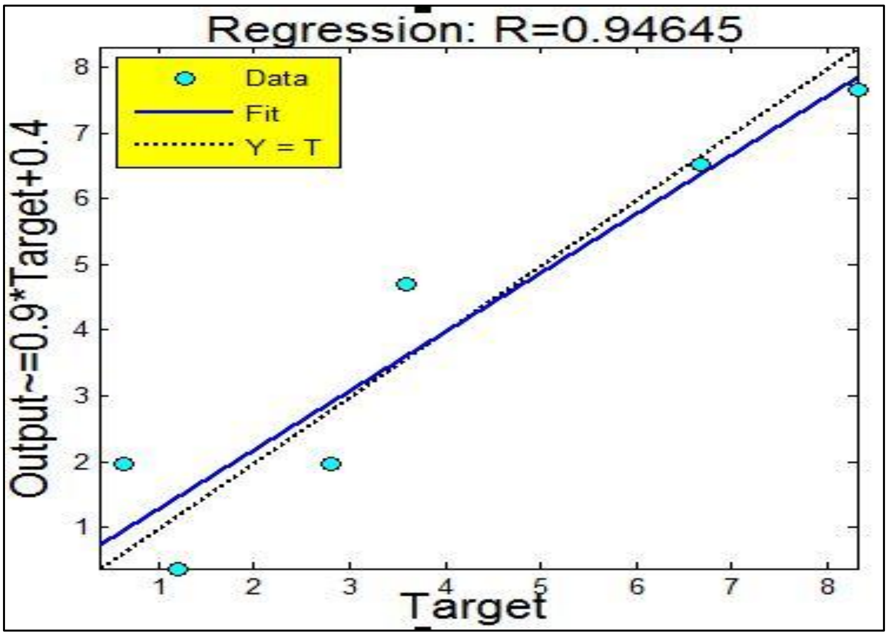

FIGURE 19 Regression for modified Langmuir model @ 80^oC

4.1.3.1. Modified Langmuir Model Interpretation

As shown in Figure 16 and Figure 18, modified Langmuir equation created interestingly better results. Compare to lack of fit for original Langmuir model, the modified version of Langmuir equation shows better good match between model output and observations.

4.1.3.2. Regression of Modified Langmuir Model

The regression for modified Langmuir model also increase toward 1 significantly after the sulfonation degree is added into the equation as shown in Figure 17 and Figure 19. In cases, 20^{o}C and 80^{o}C, the regression value are much closer to 1. It shows the superiority of modified Langmuir model.

4.1.3.3. Root Square Mean Error (RSME)

Table 13 shows the coefficient estimations of the correlation for modified Langmuir isotherm at temperature, 20^{o}C. The initial value extracted from the previous study [47] and iteration process by using “nlfit” function of MATLAB is carried out to estimate final value model coefficients.

TABLE 13 Estimated coefficient of fitting parameters

Parameter	initial Values	Final Value
a_{p1}	74.4	142443.6651
a_{p2}	0	4393519.648
b_3	1417	60196.76297
a_4	1	-12778.18906

From the estimated coefficient for temperature at 20^{o}C , the RMSE value is small which is 0.8697, it shows it is high measure of accuracy which mean the differences between values predicted by a model and the values actually observed from the experimental job has been minimized. Thus, the result is remarkable.

Table 14 shows the coefficient estimations of the correlation for modified Langmuir isotherm at temperature, 80^{o}C. The initial value extracted from the previous study [47] and iteration process by using “nlfit” function of MATLAB is carried out to estimate final value model coefficients.

TABLE 14 Estimated coefficient of fitting parameters

Parameter	initial Values	Final Value
a_{p1}	74.4	311411.7031
a_{p2}	0	-302656.6077
b_3	1417	39065.59034
a_4	1	-8915.423391

From the estimated coefficient for temperature at 80^oC , the RMSE value is small which is 0.899, it shows it is high measure of accuracy which mean the differences between values predicted by a model and the values actually observed from the experimental job has been minimized. Thus, the result is remarkable.

Prediction and Actual Adsorbed Polymer Concentration ($\hat{C}_p$)

Temperature @ 20^oC

Table 15 shows the diffrences between observed values and prediction of modified Langmuir model for temperature at 20^{o}C. Column of Observation show retention amount which has been measured in laboratory after converting to the desired unit need for apply in the model.

TABLE 15 Retention amount for observation and prediction of the model (at 20^{o}C)

		Observation	Prediction of the model
Retention	Cp(ppm)	Ĉp(ppm)	Ĉp(ppm)
93.43	5000	5.591683808	5.146299897
111.46	5000	6.670752486	5.973609942
29.48	5000	1.764352666	3.448110375
58.64	5000	3.509547482	4.27542042
32.45	5000	1.942104268	0.900826092
38.96	5000	2.331721196	1.728136136
7.36	5000	0.440490258	0.900826092
1.29	5000	0.077205522	0.900826092
3.23	5000	0.193313028	1.728136136
6.76	5000	0.404580741	-0.58508974
16.48	5000	0.986314605	0.242220305
52.49	5000	3.141477066	3.103533174
108.92	5000	6.518737405	6.207668348
124.2	5000	7.433221129	7.034978393

Temperature @ 80°C

Table 16 shows the diffrences between observed values and prediction of modified Langmuir model for temperature at 80°C. Column of Observation show retention amount which has been measured in laboratory after converting to the desired unit need for apply in the model.

TABLE 16 Retention amount for observation and prediction of the model (at 80°C)

		Observation	Prediction of the model
Retention	Cp(ppm)	Ĉp(ppm)	
111.7	5000	6.685116113	6.532757644
60	5000	3.590941879	4.707023382
46.8	5000	2.800936878	1.968421989
10.5	5000	0.628416691	1.968421989
20	5000	1.196983492	0.37090451
139	5000	8.31897602	7.673841558

4.1.4. Beta Value

Beta value is the covalent coefficient that take into account the effect of salinity in Langmuir equation. The value for beta (ß) changes for different type of polymer. For sulfonated polyacrylamide polymer, the best approximation for beta value is 4 as the root mean square error (RMSE) is the lowest as shown in the figure 20. This condition is applied to both cases for temperature of 20°C and 80°C.

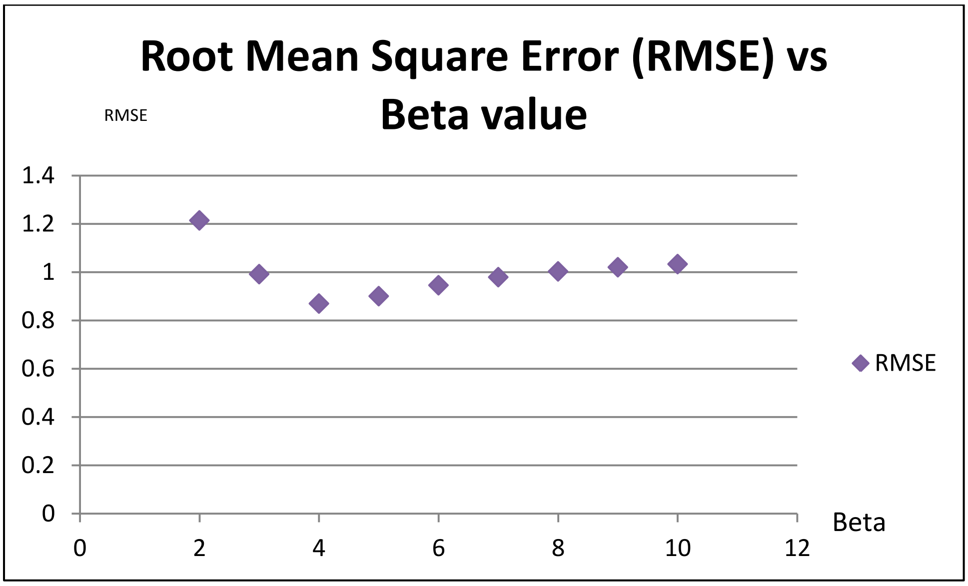

FIGURE 20 Root Mean Square Error (RMSE) vs beta value

4.2. Summary of Main Results

Study of developed modified model proves that retention of sulfonated polyacrylamide is predictable only when effect of sulfonation degree has been considered, as shown in figure 17 and 19. The prediction ability of the modified model is greatly increased with an addition of sulfonation degree parameter into the Langmuir model. The influence of sulfonation degree on solfonated polyacrylamide polymer is explicit. Thus in calculating the retention of sulfonated polyacrylamide polymer in porous media, the effect of sulfonation degree should be taken into account.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

This report presents an investigation of polymer adsorption phenomena and also modelling in the polymer flooding process. The main conclusions can be summarized as follows:

.

i) Sulfonation degree has great effect on the retention of sulfonated polyacrylamide compared to the other parameters. Based on p-value result, sulfonation degree has significant effect on retention of sulfonated polyacrylamide. The parameter must be taken into account in measuring polymer adsorption through porous media.

ii) For sulfonated polyacrylamide polymer, modified Langmuir adsorption model should be used to determine the retention amount instead of the Langmuir model.

5.2. Recommendations

Based on what we achieved by this study we recommend that:

i) The modified model presented in this study may also be tested for different sets of other sulfonated polyacrylamide data from literatures.

ii) The developed model which has been presented in this study still can be modified by incorporating other parameters into the model, If more precise data is needed. Of course, to achieve this goal, more observation is needed.

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APPENDICES

Appendix 1

Synthetic Seawater Composition Containing the Main Ions with the Same Salinity of Seawater—Grams of Salts in 1 kg Solvent

Salt	Amount in g kg^{-1} solvent
NaCl	25.0
$MgCl_2 \cdot 6H_2O$	11.1
$CaCl_2 \cdot 2H_2O$	1.7
KCl	0.7

Appendix 2

Polymers Characteristics

Polymer[a]	Molecular weight (Million Dalton)	Sulfonation degree (Mole %)
AN105	6	5
AN113	8	13
AN125VLM	2	25
AN125	8	25
AN125VHM	12	25
AN132	8	32
HPAM	8	–

[a] All studied polymers were supplied by SNF FLOERGER.

Mathlab coding for temperature of 20^oC

```
%% Effect of SD has not been taken into account%%%%%%%%%%%%%%%%%%%%
clc
clear all
trnRMSE1=5000;
load predictionhs
n1=dataintrain(:,4);
n2=dataintrain(:,5);
n3=dataintrain(:,6);
for B_Value= 4
CSE=(n1+(B_Value-1).*n2)./n3;
dataintrain_n(:,1)=dataintrain(:,3);
dataintrain_n(:,2)=CSE;
dataintrain_n(:,3)=dataintrain(:,7);
for i=1:1000;
opts = statset('nlinfit');
opts.MaxIter = 100000;
opts.TolFun = 1e-20;
[beta,r,J,COVB,mse] = nlinfit(dataintrain_n,retention,@hasa_sd,beta,opts);

b1 = beta(1);
b2 = beta(2);
b3 = beta(3);
b4=  beta(4);

% Error and prediction ability for traing data set%%%%%%%%%%
x1_tr = dataintrain_n(:,1);
x2_tr = dataintrain_n(:,2);
x3_tr = dataintrain_n(:,3);
Prediction_train = (((b1+(b4.*x3_tr)+(b2.*x2_tr)).*x1_tr))./(1+(b3.*x1_tr));
TrainResult=[retention,Prediction_train,r];

% trnMSE=mse(retention-Prediction_train)
trnRMSE=norm(Prediction_train-retention)/sqrt(length(Prediction_train))

% %%%%%%%%%export data from  matlab to
Excel%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
logfilename='TRACE20.txt';
Export=fopen (logfilename,'a');
fprintf(Export,'\n   %f;%f',B_Value,trnRMSE);
fclose(Export);
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%
if trnRMSE<trnRMSE1;
   save BestHNet_SD_20
end;
if trnRMSE<trnRMSE1;
   trnRMSE1= trnRMSE;
end;
end
end;

clc
clear all
load BestHNet_SD_20
figure (1)
plot(retention)
hold on
plot(Prediction_train,'o')
Title('Best Prediction Ability of  Modified Langmuir Model for 20 C ');
xlabel('input index');
legend('actual','prediction');

error_train=((retention-Prediction_train)./(retention))*100
plotregression(retention,Prediction_train);
%% Effect of SD has not been taken into account%%%%%%%%%%%%%%%%%%
clc
clear all
mse1=1000;
trnRMSE1=5000;
load predictionhs
n1=dataintrain(:,4);
n2=dataintrain(:,5);
n3=dataintrain(:,6);
for B_Value= 4
CSE=(n1+(B_Value-1).*n2)./n3;
dataintrain_n(:,1)=dataintrain(:,3);
dataintrain_n(:,2)=CSE;
for i=1:1000;
opts = statset('nlinfit');
opts.MaxIter = 100000;
opts.TolFun = 1e-20;
[beta,r,J,COVB,mse] = nlinfit(dataintrain_n,retention,@hasa,beta,opts);

b1 = beta(1);
b2 = beta(2);
b3 = beta(3);
```

```
% Error and prediction ability for traing data set%%%%%%%%%
x1_tr = dataintrain_n(:,1);
x2_tr = dataintrain_n(:,2);
Prediction_train = (((b1+(b2.*x2_tr)).*x1_tr))./(1+(b3.*x1_tr));
TrainResult=[retention,Prediction_train,r];

% trnMSE=mse(retention-Prediction_train)
trnRMSE=norm(Prediction_train-retention)/sqrt(length(Prediction_train))

% %%%%%%%%export data from  matlab to
Excel%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% logfilename='TRACE.txt';
% Export=fopen (logfilename,'a');
% fprintf(Export,'\n   %f;%f;%f;%f',i,AAPET1,AAPET2,mse);
% fclose(Export);
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%
if trnRMSE<trnRMSE1;
   save BestHNet_NSD_20
end;
if trnRMSE<trnRMSE1;
   trnRMSE1= trnRMSE;
end;
end
end;

clc
clear all
load BestHNet_NSD_20
figure(2)
plot(retention)
hold on
plot(Prediction_train,'o')
Title('Best Prediction Ability of Langmuir Model for 20 C');
xlabel('input index');
legend('actual','prediction');
error_train=((retention-Prediction_train)./(retention))*100
plotregression(retention,Prediction_train);
```

Coding for temperature of 80°C

```
%% Effect of SD has not been taken into account%%%%%%%%%%%%%%%%%%%%
clc
```

```
clear all
trnRMSE1=5000;
load predictionhs
n1=dataintrain(:,4);
n2=dataintrain(:,5);
n3=dataintrain(:,6);
for B_Value= 2;1;10;
CSE=(n1+(B_Value-1).*n2)./n3;
dataintrain_n(:,1)=dataintrain(:,3);
dataintrain_n(:,2)=CSE;
dataintrain_n(:,3)=dataintrain(:,7);
for i=1:1000;
opts = statset('nlinfit');
opts.MaxIter = 100000;
opts.TolFun = 1e-20;
[beta,r,J,COVB,mse] = nlinfit(dataintrain_n,retention,@hasa_sd,beta,opts);

b1 = beta(1);
b2 = beta(2);
b3 = beta(3);
b4=  beta(4);

% Error and prediction ability for traing data set%%%%%%%%%
x1_tr = dataintrain_n(:,1);
x2_tr = dataintrain_n(:,2);
x3_tr = dataintrain_n(:,3);
Prediction_train = (((b1+(b4.*x3_tr)+(b2.*x2_tr)).*x1_tr))./(1+(b3.*x1_tr));
TrainResult=[retention,Prediction_train,r];

% trnMSE=mse(retention-Prediction_train)
trnRMSE=norm(Prediction_train-retention)/sqrt(length(Prediction_train))

% %%%%%%%%export data from  matlab to
Excel%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
logfilename='TRACE80_test.txt';
Export=fopen (logfilename,'a');
fprintf(Export,'\n   %f;%f;%f;%f;%f;%f',b1,b2,b3,b4,B_Value,trnRMSE1);
fclose(Export);
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%
if trnRMSE<trnRMSE1;
   save BestHNet_SD_80
end;
if trnRMSE<trnRMSE1;
```

```
    trnRMSE1= trnRMSE;
end;
end
end;

clc
clear all
load BestHNet_SD_80
figure (1)
plot(retention)
hold on
plot(Prediction_train,'o')
Title('Best Prediction Ability of  Modified Langmuir Model for 80 C');
xlabel('input index');
legend('actual','prediction');

error_train=((retention-Prediction_train)./(retention))*100
plotregression(retention,Prediction_train);
%% Effect of SD has not been taken into account%%%%%%%%%%%%%%%%%%
clc
clear all
trnRMSE1=5000;
load predictionhs
n1=dataintrain(:,4);
n2=dataintrain(:,5);
n3=dataintrain(:,6);
for B_Value= 2;1;10;
CSE=(n1+(B_Value-1).*n2)./n3;
dataintrain_n(:,1)=dataintrain(:,3);
dataintrain_n(:,2)=CSE;
for i=1:1000;
opts = statset('nlinfit');
opts.MaxIter = 100000;
opts.TolFun = 1e-20;
[beta,r,J,COVB,mse] = nlinfit(dataintrain_n,retention,@hasa,beta,opts);

b1 = beta(1);
b2 = beta(2);
b3 = beta(3);

% Error and prediction ability for traing data set%%%%%%%%%
x1_tr = dataintrain_n(:,1);
x2_tr = dataintrain_n(:,2);
Prediction_train = (((b1+(b2.*x2_tr)).*x1_tr))./(1+(b3.*x1_tr));
TrainResult=[retention,Prediction_train,r];

% trnMSE=mse(retention-Prediction_train)
```

```
trnRMSE=norm(Prediction_train-retention)/sqrt(length(Prediction_train))
 % %%%%%%%%export data from  matlab to
Excel%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% logfilename='TRACE.txt';
% Export=fopen (logfilename,'a');
% fprintf(Export,'\n   %f;%f; %f%f',i,AAPET1,AAPET2,mse);
% fclose(Export);
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%
if trnRMSE<trnRMSE1;
   save BestHNet_NSD_80
end;
if trnRMSE<trnRMSE1;
   trnRMSE1= trnRMSE;
end;
end
end;
 clc
clear all
load BestHNet_NSD_80
figure(2)
plot(retention)
hold on
plot(Prediction_train,'o')
Title('Best Prediction Ability of Langmuir Model for 80 C');
xlabel('input index');
legend('actual','prediction');
error_train=((retention-Prediction_train)./(retention))*100
plotregression(retention,Prediction_train);
```